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Scott- here's a hard copy version of the email I sent out.

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September 19, 1997

Ms. Susan Zazzali
U. S. Environmental Protection Agency
301 S. Park
Federal Building Drawer 10096
Helena, Montana 59626-0096

Subject: **Summary of Groundwater Comments, ASARCO East Helena Smelter
REPA Contract No. 68-W4-0004, Work Assignment No. R08024**

Dear Ms. Zazzali:

At the request of the US. Environmental Protection Agency (EPA), Tetra Tech EM Inc. (EMI) has compiled a summary of comments that address groundwater issues at the ASARCO East Helena Smelter site. Some comments are based on conclusions and recommendations in the groundwater evaluation report (Tetra Tech EM, Inc. 1997) recently submitted to EPA. Other comments are based on EMI's evaluation of the May 1997 organic sampling results for monitoring wells DH-27 and DH-28. In addition, EMI has restated some comments on the Post-Remedial Investigation (RI) Well and Surface Water Monitoring Report (Hydrometrics 1995) that were previously provided to EPA by CH2M Hill. The comments are divided into general and specific comments. General comments address general groundwater issues and the post-RI monitoring report (Hydrometrics 1995). Specific comments address only the post-RI monitoring report (Hydrometrics 1995).

General Comments

1.   It is recommended that the post-RI monitoring report be updated. The current report (Hydrometrics 1995) does not reflect the present status of site conditions and does not accurately present current groundwater conditions. The report's most recent data (1994) and data interpretations are approximately 3 years old. During this 3 year period, numerous remedial actions have been implemented at the site, significant changes in site groundwater conditions have occurred, and a large amount of additional monitoring data has been gathered.

    A revised post-RI monitoring report would provide the ~~data base~~ *baseline data* for groundwater characterization. The characterization of site groundwater should include: (1) describing current groundwater conditions; (2) evaluating the effectiveness of remedial actions to date; (3) determining the presence and impact of unremediated source areas; and (4) predicting groundwater conditions in the future if no further action or specific remedial actions were to occur. The updated report should include a presentation and discussion of monitoring data through 1997 and should include the additional and revised data presentation and analysis described in the comments below.

2.   Arsenic concentrations in the central portion of the groundwater plume have generally decreased in the past 4 years. These decreases appear to be the result of source removal actions at the site. The arsenic plume boundary has remained relatively stationary between 1990 and 1994 and no significant changes to the plume boundary have occurred between 1994 and 1996. However, groundwater still contains elevated arsenic concentrations in numerous monitoring wells: some have shown recent decreases in arsenic concentrations (DH-12, DH-17, DH-24 and others); some have had unexplained spikes or fluctuations in arsenic concentrations (DH-27, DH-28, DH-29, EH-51, and others); and some have indicated recent increases in arsenic concentrations (DH-10, DH-21, APSD-2,

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and EH-60). Some discussion regarding the reasoning for all three of these conditions should be provided, focussing primarily on the causes of the latter two conditions. Such explanations should be sought in the associated historical water chemistry data and in conjunction with relevant site activities so that groundwater concentrations at these locations can be better understood. In addition, the large spikes in arsenic concentration should be evaluated and the affect of these transients on downgradient portions of the plume should be determined.

3.   The current post-RI monitoring report does not clearly summarize what has happened to the groundwater system over the long timeframe that has been monitored. Given the extent of remedial work that has been conducted within the plant over the last 6 years to mitigate groundwater impacts, it is important to measure the success or failure of those actions. Therefore, monitoring results and trends should be presented in conjunction with summaries of recent remedial actions in order to understand what has happened to the groundwater systems over the time period due to these remedial actions. The presentation should identify and explain anomalous conditions and attempt to identify any remaining arsenic source areas.

4.   Organic constituents have been detected in subsurface soils and groundwater samples at several locations in the central portion of the plant site, including wells DH-12, DH-27, and DH-28. Organic constituents have also been detected in downgradient, off-site wells EH-60 and EH-61. The presence of organic contamination in site groundwater could be significantly affecting arsenic attenuation and release processes in the aquifer. Organic contamination can result in reducing conditions in the aquifer, which increases the mobility of arsenic, and it is possible that this contamination could be related to the anomalous arsenic concentrations at wells DH-21 and EH-60. In addition, a future release of organic constituents at, or downgradient of, the site could result in the movement of the arsenic plume.

An analysis of the interrelationship of inorganic (particularly arsenic) and organic contamination should be provided. This analysis should be included as part of a fate and transport analysis of the site geochemical system in order to understand the long-term stability and migration of the arsenic plume. Correlations between inorganic and organic constituents should be presented. A map showing any spatial or other relationship between arsenic and inorganic constituents should be produced.

5.   The types of organic analysis being conducted on groundwater samples at the site have not been consistent and, therefore, do not allow for uniform comparison of sampling results. It would be helpful if uniform organic analysis were conducted on samples from all wells that have indicated historical organic contamination. A uniform set of analyses may include diesel range organics (DRO); gasoline range organics (GRO); carbon scans; benzene, toluene, ethylbenzene, and xylenes (BTEX); volatile organic compounds; and semivolatile organic compounds. Uniform analyses should be compared to determine if the contamination is from one or multiple sources. Wells indicating organic contaminants should be sampled for organics at the routine 6-month intervals to better understand the significance of these constituents.

6.   Updated arsenic time trend charts (through 1997) should be prepared and an analysis of recent arsenic trends should be provided. Time-change maps of arsenic, arsenic speciation, iron, manganese, and perhaps sulfate between sampling events (or at least seasonally) should be prepared to provide a clearer presentation of time trends across the site. The change maps can be constructed by subtracting the latest sample result for each season from earlier sample results (with dates shown adjacent to the value) and contouring the results.

7.   Normal statistical charts (instead of nonparametric box and whisper plots) should be prepared for at least arsenic, ratio of arsenic III to arsenic V, iron, manganese, redox potential (Eh), pH, and, if wanted, sulfate for each well. A normal summary statistics chart showing each data value plotted versus the mean and both one and two standard deviations compared with time from the currently available data should be prepared with all the charts shown on a

single page for each well.

8.　Dissolved oxygen is useful for the gross depiction of the oxidation state of the groundwater, but Eh is a much more sensitive measurement showing this trend (assuming that the Eh is determined in a closed cell during sample collection). Eh also is by far the better indicator of reducing conditions and as such a better measure of area affected by organic carbon and its recovery to oxidized conditions. A discussion of any relevant Eh data should be provided to better define the apparent groundwater oxidation.

9.　Based on the available arsenic data, some well locations could be eliminated from future sampling events or reduced in sampling frequency. The frequency and locations of groundwater well sampling should be assessed and specific modifications proposed, if desired.

10.　Reliable arsenic speciation at this site is critical with respect to mobility and toxicity. The reduced form of arsenic (AsIII) is much more mobile and toxic than the oxidized form (AsV). However, the historical arsenic speciation data appear to have low precision and poor accuracy. The quality of the arsenic speciation data should be evaluated to determine the impact on AsIII and AsV quantification. Geochemical fate and transport conclusions based on AsIII to AsV ratios could be unreliable if speciation values are highly variable.

11.　If arsenic speciation data is indeed useful (see general comment 10 above), a more thorough discussion and mapping of groundwater arsenic speciation and a more thorough discussion of the potential interrelationships among inorganic constituents, organic constituents, and pertinent geochemical parameters should be provided. It is important to provide an accurate picture of arsenic attenuation in the aquifer. This can be gaged by the relative amounts of the oxidized and reduced forms of arsenic and by the relative increases or decreases in the ratio of these arsenic forms.

12.　There is considerable discrepancy between the dissolved arsenic and the arsenic speciation concentrations for surface water locations PPC-5, PPC-101, PPC-102, and PPC-103. It should be determined which are correct and the report figures and text should be revised accordingly.

13.　A water balance analysis should be conducted in order to better understand the relationship of surface water, precipitation recharge, site groundwater, and the fluctuations in arsenic concentrations in many site wells.

14.　Figures with negative scales and minus concentrations are confusing and should not be used. Negative concentrations should not be shown. If necessary, a different arithmetic scaled graph should be used to show the lower concentration trends, or a logarithmic scale can be used.

15.　Correlation analysis should be at least partially reconsidered based on data distribution. Some of the best correlations involve a relatively tight cluster of data points with only one or two outlier data points (either extremely high or extremely low) that define the population. These correlations need to be dropped, have some form of outlier test applied to the population before correlating parameters, or have the one or two points deleted to see if this correlation is significantly different. It is preferable to use outlier testing because outliers are of considerable interest in this type of investigation, particularly when a comparison can be made between pre-and post-remedial groundwater chemistry.

Specific Comments

1.　__P. 4-1, last sentence and Figure 4-4.__ The means for the arsenic speciation should also be described here. There is a significant difference in the speciation means shown on Figure 4-4. For example, AsV increases in groundwater from wells DH-21 and DH-28 in proportion to other wells. Chloride should be removed from the arsenic plot of means and either included in the plot along with specific conductance, sulfate, and total dissolved solids (TDS), or

dropped. However, the relationship among both arsenic and chloride and either specific conductance or TDS for groundwater from well DH-29 appears to be anomalous compared with values for other groundwater samples. This anomaly should be investigated and, if possible, explained.

2.   P. 4-6, first paragraph and Figure 4-5. A pH scale should be added to the right-hand side of the upper plot that allows pH to be plotted across the full scale of the plot. It is difficult to discern the pH let alone its relationship with the metals. The potential relationship or lack thereof between pH and arsenic also should be described. Dissolved copper and lead should be deleted from the plot since they are shown on the bottom plot to be much lower in dissolved concentration than either the zinc or the cadmium. The relative association between the two pairs copper/lead and zinc/cadmium is common in mining sites and these associations are related to both source and mobility. A plot of dissolved iron relative to pH, arsenic, copper, and lead should be provided.

3.   P. 4-6, Section 4.2. The text should describe the difference between the median and the mean. The previous plots should be plotted against the median also because the mean, standard deviation, and variance are strongly influenced by the extreme concentrations but the median is not because it is simply the middle concentration of the ranked population. The percentiles and whiskers do not show variance/standard deviation in their commonly defined form. The whiskers instead show outliers above and below the 25 and 75 percent of the concentration values and do not assume a normal distribution. For example, in Figure 4-6, the relationship between TDS and arsenic is not the same as the mean values on Figure 4-4 and the whiskers dominantly show high concentration outliers, not low concentration outliers. Also, the position of the medians in the 25 to 75 percent range of concentration values is highly variable. Medians are commonly better measures of central tendency than means for trace constituents in contaminated sites because they are not influenced by either extremely high or extremely low concentrations.

4.   P.4-12, second paragraph, first sentence and Figure 4-10. This section should be revised to include a tabulated list and a map of locations where arsenic concentrations have decreased, remained essentially constant, or increased. Many of the individual wells on Figure 4-10 are difficult to discern because the symbols are not distinct or overlap. This, and similar figures should be revised for readability.

Groundwater arsenic concentrations from monitoring well DH-60 show a definite increase over time, and some explanation needs to be offered as to the increase. Groundwater from well DH-54, however, appears to indicate a strong degree of variability and an explanation of this variability should be provided.

5.   P. 4-12, third paragraph and Figure 4-12. The nomenclature for water levels is confusing. It would be better to illustrate a water level using the elevation of the water level, which then allows the water levels to be compared from well to well. A rising water level would then be a positive trend.

The description in this section suggests that the water level generally rose in the area. This change should be clarified in the text and an explanation for the increase in water levels provided. The trend plots in Appendix F actually indicate that the water level in many wells changed very little during the period of record. A tabulated list of precipitation for the years of interest would be helpful and should be provided in the introduction. It is important to be able to distinguish between the changes due to remedial actions and those due to dilution. It is also important to know how the groundwater system responds to changes in recharge and use across the area. The difference maps suggested in the general comments would help illustrate how and where the groundwater gradient changes may be affecting the arsenic plume.

6.   P.4-17, second paragraph, second sentence. The text should explain why, and to what degree, the water level in DH-12 does not correspond to the water levels in the other wells. The text should indicate, as pointed out in the above comment, that many of the water levels do not change very much or change in only one to two

measurements over a period of time.

7.   <u>P.4-17, last paragraph</u>. This section should provide a more quantitative determination of the degree of dilution at each well caused by the increased recharge. The amount of dilution should be related to both spring versus fall and the depth of the screen beneath the water table. The arsenic concentration itself should decrease with depth below the water table.

8.   <u>P.4-20, Section 4.5.2, Correlations, first paragraph</u>. Arsenic-sulfate correlations for wells DH-19, APSD 3, DH-6, EH-52, and EH-54 depend on a cluster of data in a limited concentration range with only a single extreme data point (typically sulfate concentration) that controls the entire correlation. This data point should be eliminated from each of the data sets and the correlations recalculated. If the correlation is not significantly changed then the conclusions described in the text are correct. However, the plots in Appendix G indicate that correlations, at least for these wells, will be considerably poorer and may reverse in trend. Data sets with this clustering and only one or two much higher or lower data points should be reappraised.

9.   <u>P. 4-20, Section 4.6</u>. Difference maps of both chemical constituents (at least arsenic and sulfate) and potentiometric surface should be constructed to allow a quantitative assessment of temporal and spatial changes.

10.   <u>P. 4-22, Section 4.7</u>. A tabulated list of organic constituents above their detection limit and their concentrations for the wells should be compiled and described. If a well contains one or more detected organic constituents, a column with the sum of organic concentrations for each sampling event and over the period of sampling should be provided and compared with the arsenic concentration distribution.

11.   <u>P. 4-24, last sentence</u>. An explanation of EH-60 arsenic and dissolved oxygen conditions should be provided here. A low dissolved oxygen concentration suggests a reducing condition in groundwater that would allow arsenic to be mobile. Arsenic is mobile because iron is a poor adsorption media under reducing conditions (poor attenuation of arsenic because of poor adsorption on ferric oxyhydroxide). An explanation of whether the arsenic mobility and low dissolved oxygen are related to organic contamination at this location should also be provided.

12.   <u>P.5-3, Figure 5-2</u>. The dissolved arsenic correlation for surface water monitoring station PPC-8 should be reevaluated. A single high concentration point may control the correlation coefficient and least square fit line. If this one data point is removed, the trend line will be much flatter, probably change direction, and will closely resemble the trend (and correlation) for surface water monitoring stations PPC-7 and PPC-3.

A copy of these comments has been sent to you via electronic-mail in WordPerfect 6.1. Please call Chris Reynolds or me at (406) 442-5588 if you have any questions or require further assistance.

Sincerely,

Brian Antonioli, P.E.
Project Manager

Attachment: references

cc: EMI file

REFERENCES

Hydrometrics. 1995. ASARCO East Helena Post-RI Well and Surface Water Monitoring Report (1990-1994). Prepared for ASARCO, Inc. September.

Tetra Tech EM, Inc. 1997. ASARCO East Helena Smelter, Evaluation of Groundwater Data. Prepared for the US. Environmental Protection Agency. Jul